UNEXPLORED PRODUCTS FROM
REACTIONS OF LOW-RANK COAL IN AQUEOUS SYSTEMS

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INTRODUCTION

Processing of coal in aqueous systems has been investigated for a variety of purposes. The aqueous processing conditions can be divided into three temperature regimes. Temperatures over $375^\circ C$ are considered to be liquefaction conditions. The liquefaction of coal in water and carbon monoxide at $400^\circ C$ was demonstrated in 1921 by Fischer and Schrader [1]. Appell applied aqueous processing to lignites and Bruceton coal in 1968 [2]. An organic vehicle was also added in much of their study. Further development of aqueous carbon monoxide (CO-Steam) processing was conducted at the Grand Forks Energy Technology Center [3]. Stenberg has reported the processing of low-rank coals in water-hydrogen sulfide mixtures [4]. The chemistry of aqueous conversions of bituminous coals at $400^\circ C$ has been investigated by Ross [5] and Ruether [6]. Supercritical aqueous systems have also been investigated for low-rank coal liquefaction [7]. Temperatures less than $300^\circ C$ have been studied for coal activation in staged processing [8,9]. Intermediate temperatures (300 to $370^\circ C$) are used in processes such as hot water drying of low-rank coals [10].

Our studies were directed toward elucidating the transformation of oxygen functional groups during processing of low rank coals. This paper reports the results from a matrix of reactions conducted in aqueous systems in the intermediate temperature range (300 to $325^\circ C$). The objectives were to determine the extent of conversion with an emphasis on decarboxylation and dehydration reactions under these mild conditions and to investigate the cleavage of oxygenated organic compounds, such as phenolics and ketones, from the coal structure. The effects of phase transfer catalysts in improving the conversion were studied. Also, the question of whether a submicron-particle-size dispersion of the coal in an alkaline medium has any effect on reactivity in the liquefaction was investigated.

In this intermediate temperature range, the changes in the coal were extensive enough so that conversion to soluble and volatile products was obtained, and detailed analyses of the products were carried out. The products were in some cases different from those obtained at higher temperatures. Some of these products are not stable at 375°. In conducting experiments at the intermediate temperatures, there is less uncertainty about whether products resulted from primary or secondary reactions.

EXPERIMENTAL

A matrix of reactions were carried out under different conditions with a high sodium Beulah (ND) lignite [11]. The lignite (850 micron size) was mixed with the aqueous medium in a 1:25 ratio. Reactions were carried out in a 300 ml Parr bomb reactor with magnetic stirring. The reactor was heated at the desired temperature (with cold charge) for one hour. At the end of the reaction period, the reactor was cooled to room temperature and the product

gases removed. The solid product was recovered by filtration. Percent conversion was reported as 100 minus the percent of the insoluble solid recovered (mf basis).

The basic filtrate was extracted with ether to give an ether-soluble extract of neutral components. Acidification of the filtrate and extraction with dichloromethane gave the base-soluble fraction (mainly phenolics and lactones). The physical and product yield data are given in Table 1. Along with various yield comparisons, the reaction products were examined with solid state ^{13}C NMR, PAS-FTIR, and GC/FTIR/MS (12). Analyses of catechols were performed with an HPLC method.

One experiment involved testing a colloidal dispersion in aqueous 5% sodium hydroxide. The dispersions were made by blending the as-received coal with the aqueous base at high speed at ambient temperatures with a kitchen-style blender (11). These dispersions are very stable and are resistant to separation by centrifugation as well as filtration.

RESULTS AND DISCUSSION

The reaction of Beulah lignite in water (no reducing agent or catalyst) at 325°C was examined first as the basis for further investigations. Duplicate runs gave very low conversions (21%). The PAS-FTIR spectrum of the coal residue showed that some loss of carboxylic acids groups had occurred, and a small residual pressure of carbon dioxide was obtained as a result of the thermal decarboxylation. The ^{13}C NMR spectrum of the residue showed it to be considerably deficient in aliphatic carbons in comparison with that of the unreacted Beulah. Analysis of the soluble products showed that the phenolic fraction consisted mainly of phenol and guaiacol, with smaller amounts of cresols and the series of methyl-, ethyl-, and propylguaiacol, and even smaller amounts of the other alkylphenols commonly found in coal pyrolysis products. This distribution of the phenolics, with the guaiacols in abundance, is unusual and therefore remarkable. Traces of catechols were also present. The portion of the coal structure which is most like lignin is evidently the most easily cleaved under neutral conditions. The neutral product fraction consisted mainly of cyclic ketones, such as substituted cyclopentanones and cyclopentenones, and small amounts of alcohols (13). These polar organic compounds were qualitatively analyzed with the GC/FTIR/MS.

Aqueous processing was next investigated by adding a mixture of formic acid and sodium formate to the suspension of coal in water and heating at 325° for one hour. A significant increase (doubling) in the conversion was observed. A residual pressure of 200 psi was observed in the reactor after cooling. The gas contained CO, formed from the decomposition of formate, and CO_2 from decarboxylation and possibly the water gas shift reaction. FTIR spectroscopy of the unconverted residue confirmed the loss of carboxylic acid groups. The weight of soluble products was 75% of that predicted by the conversion data. In addition to the CO_2 from decarboxylation, water may be lost from the coal structure via dehydration reactions. The soluble products from the reaction were the phenolics and ketones. In this experiment with the added formate, the distribution of phenolics was more typical of low-rank coal pyrolysis or high temperature liquefaction product, with very small amounts of guaiacol and the alkyl-substituted guaiacols and large amounts of cresols and alkylphenols.

A similar liquefaction reaction was performed with the formate under basic conditions (5% aqueous NaOH). The conversion after heating at 325°C was about the same as that obtained in the formic acid/formate system above. Less decarboxylation was observed in this case. This finding is consistent with that observed at higher temperatures, that base retarded the decarboxylation, and acid conditions promoted the decarboxylation.

The phenolic products were typical of pyrolysis products with small amounts of guaiacols. Another class of compounds was found in significant amounts in these products from the alkaline reaction conditions. A series of lactones was observed in the material obtained by acidification of the base-soluble fraction. In the basic solution, the lactones are present in the hydroxy acid carboxylate form, which then closes up to the lactone during acidification. Four lactones were identified by matching mass spectra and infrared spectra (13). The identified lactones are γ-butyrolactone, α-methyl-γ-butyrolactone, γ-valerolactone, and γ-caprolactone. These lactones were absent in the previous experiments, which were run under neutral and acidic conditions.

A study of reactivity of colloidal dispersions of lignite was performed for comparison with the reactivity of the larger particle coal systems described above. The submicron dispersion of Beulah lignite in aqueous sodium hydroxide was prepared and heated with sodium formate at 325°C. The product yield data indicated that the conversion was roughly the same as that obtained from particulate coal suspensions in base under identical liquefaction conditions. It was concluded that conversion is dependent upon reaction temperatures, times, reducing agents, and catalysts and is independent of the particle size of the coal. This is probably because either the coal breaks down sufficiently or the reactions are not diffusion controlled.

The reaction of Beulah lignite at 325°C in aqueous sodium hydroxide, with no formate present, was also investigated. The conversion dropped considerably and was comparable to that obtained for the reaction in water with no reducing agent. Products were similar to those obtained in the alkaline formate reaction.

To study the effects of temperatures on conversion, decarboxylation and nature of products being formed, several reactions were carried out with the alkaline lignite dispersion with added formate at temperatures of 250 and 300°C. The conversions at 250°C were very poor (0 and 7%) and the conversion at 300° (34%) was considerably lower than that obtained at 325°C. FTIR studies indicated that very little decarboxylation occurred at temperatures less than 300°C. Phenols were the major products as before.

Several possible coal structures may be considered as precursors for the lactone products obtained. The lactones were obtained under basic conditions even in the absence of formate; thus, a hydrolytic cleavage would seem to be more probable than a reductive cleavage. Hydrolysis of an ester linkage could liberate the γ-hydroxyacids at either the acid or alcohol end, or hydrolysis of a polyester could also give the hydroxyacids. Poly(β-hydroxybutyric acids) are storage polymers of bacteria, and one could speculate on the incorporation of γ-hydroxyacids into coal structures as poly(γ-hydroxyacids), as a result of the same bacterial polymerase enzyme activity during the degradation of woody material. However, attempted acid hydrolyses of coals and treatment with methoxide at lower temperatures, which are normally appropriate for

transesterification, did not give the lactone or the transesterification product, the methyl ester of the hydroxyacid. In fact, no evidence exists for the presence of esters in the low-rank coals.

A more likely possibility is an ether hydrolysis, which would involve cleavage of a bond to the oxygen of the precursor to give the lactone or the hydroxyacid, as shown in Scheme 1. This could be initiated by attack of the carboxylate anion on one side of the ether linkage (substitution mechanism) (1A) or attack of base on groups on the other side of the ether linkage (elimination mechanism) (1B, 1C).

The origin of the cyclic ketones is also intriguing, and few clues are available for deducing the precursors. The most likely possibility is that an extensive thermal rearrangement liberates the ketone. An example of such a deep-seated transformation is the production of acetone during lignin pyrolysis at similar temperatures, where aromatic carbons are incorporated into the acetone structure.

The similarity between the γ-lactone products and the muconolactones involved in the fungal metabolism of alkylbenzoic acids and catechols derived from lignin may generate an opportunity to construct new models for coal structures and the coalification process. Further work is in progress to establish this theory.

REFERENCES

1. Fischer, F.; Schrader, H. Brennst.-Chem. 1921, 2, 257-261.
2. Appell, H.R.; Wender. I. Prepr. Pap.-Am. Chem Soc., Div. Fuel Chem. 1968, 12(3), 220-224.
3. Sondreal, E.A.; Knudson, C.L.; Schiller, J.E.; May, T.H. Proceedings, 1977 Symposium on Technology and Use of Lignite, Grand Forks, ND, May, 1977.
4. Stenberg, V.I.; Nowok, J. Fuel Proc. Technol. 1986, 14, 155-159.
5. Ross, D.S.; Green, T.K.; Mansani, R.; Hum, G. Energy & Fuels 1987, 1, 287-291.
6. Ruether, J.A.; Mima, J.A.; Kornosky, R.M.; Ha, B.C. Energy & Fuels 1987, 1, 198-202.
7. Swanson, M.L.; Olson, E.S.; Diehl, J.W.; Farnum, S.A. Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 1986, 31(4), 43-55.
8. Bienkowski, P.R.; Narayan, R.; Greenkorn, R.A.; Chao, K.-C. Ind. Eng. Chem. Res. 1987, 26, 202-205.
9. Ross, D. S.; Hirschon, A. S. Proceedings, Direct Liquefaction Contractors' Rev. Mtg. 1988, Pittsburgh, PA, 328-340.
10. Baria, D.N.; Maas, D.J.; Paulson, L.E. Proceedings, Twelfth Biennial Lignite Symposium, 1983, Grand Forks, ND, 85D-861.
11. Olson, E.S.; Diehl, J.W.; Froehlich, M.L. FUEL, 1988, 67, 1053-1061.
12. Olson, E.S.; Diehl, J.W. Anal. Chem. 1987, 59, 443-448.
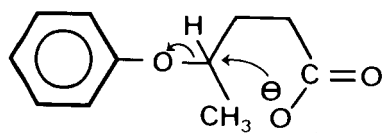13. Olson, E.S.; Diehl, J.W. J. Chromatogr. 1989, 468, 309-317.

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TABLE 1

REACTIONS OF BEULAH LIGNITE IN AQUEOUS SYSTEMS

Run Number	Solvent	Temp (°C)	Pressure (psi)	Catalyst	Conversion wt%
1.	H_2O	325	1460	NaOOCH NaOH	50
2.	H_2O	325	1450	none	21
3.	H_2O	325	1720	NaOOCH	47
4.	H_2O	325	1460	NaOOCH NaOH	50
5.	H_2O	325	1470	NaOOCH NaOH	--
6.	H_2O	325	1400	NaOOCH NaOH (Disp.)	50
7.	H_2O	325	1530	NaOH (Disp.)	23
8.	H_2O	250	460	NaOOCH NaOH	--
9.	H_2O	300	1000	NaOOCH NaOH	34

SCHEME 1

1A

1B

1C